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SALIENT FEATURES OF MELTING WHITE GLASS ENAMELS CONTAINING TITANIUM

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The effect of sodium sulfate on the properties of titanium-containing enamel is studied. It is found that introducing sodium sulfate into the initial batch during the production of titanium-containing enamel gives a whiter coating.

Glass enamel coatings, having a number of valuable user properties, are widely used in the manufacture of steel ware, sanitary ware, and household appliances. The enamel coating on such articles must possess high corrosion resistance and artistic-decorative properties — whiteness, brilliance. It is recommended that the A-1, A-2, and A-01 anatase forms of titanium dioxide (GOST 9808) and silica sand, containing no more than 0.025% iron oxides, be used in making the batch following GOST 24405–80 in order to obtain an adequate degree of whiteness of vitreous enamel coatings, since it is known that iron and chromium oxides decrease the whiteness of titanium enamels [1]. Natural silica sands, as a rule, contain more iron oxides and they must be enriched in order to be used in making white glass enamels. Enriched silica sands and titanium dioxide of the anatase form are more expensive and not always accessible to domestic manufacturers.

A complex of technological measures is required to attain a high degree of whiteness of titanium glass enamels — the raw materials must have a high purity, the frit must be made under oxidizing conditions, and it is desirable that the coatings be calcined at low temperatures, which causes anatase titanium dioxide to crystallize. As indicated in [1], higher concentrations of iron oxides in the initial materials are admissible under oxidative production conditions. In practice, when the frit is made in rotating gas furnaces oxidative conditions are not always strictly maintained; this can be judged according to the different color of the granulated material from individual meltings.

At the same time, it is known [2, 3] that the oxidation-reduction potential of the batch determines the ratio of iron

oxides with different valence of the iron in the glass and, correspondingly, the color of the glass.

As a rule, to create oxidative conditions when making glass enamels, sodium and potassium oxides are introduced as nitrate salts. However, the addition of fluorine into the enamel via sodium fluorosilicate increases the acidity of the melt and shifts the equilibrium $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$ in the direction of divalent iron. In such cases it is recommended that sodium sulfate be added to the batch to increase the oxidation-reduction potential of the glass mass [4, 5].

It is of practical and scientific interest to study the effect of small additions of sodium sulfate on the properties of titanium-containing glass enamels. Sulfur oxides, introduced as sodium sulfate, have a complex effect on glass melts — they decrease the surface tension and viscosity and clarify melts [6]. Alkali-metal sulfates, decomposing to SO_2 and O_2 during glassmaking, create oxidative conditions in the melt and give rise to a transition of iron into Fe^{3+} and titanium oxides into Ti^{4+} , which show only weak coloring power in glass. According to the data in [7], small additions of sulfates have a positive effect on the technological properties of glass enamels — they increase the spreadability and calcination interval.

The effect of sulfur oxides on the properties of glass enamels was studied for the example of composition No. 8, containing the oxides of three alkali metals and characterized by enhanced chemical stability [8]. Commercial melting of glass enamels was conducted in a rotating gas furnace, at the Santép CJSC (in Gomel'), using commercial-grade materials, R-02 titanium dioxide (GOST 9808–84), and VS-030 silica sand from the Gomel' Integrated Mining and Enrichment Plant. The founding time was 2 h 10 min with a 30 min hold-
ing period at 1300°C.

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TABLE 1

Indicator	Glass enamel	
	3rd melting	4th melting
CLTE, 10^{-7} K^{-1}	87.3	86.3
Softening onset temperature, $^{\circ}\text{C}$	550	545
Chemical stability (mass loss in 4% acetic acid), %	0.07	0.09
Coating whiteness, %	83.5	80.5

* In both cases the spreadability at 850°C was 39 mm.

Sodium and potassium oxides were introduced as nitrate salts into the batch, and lithium oxide was introduced as lithium carbonate. A definite amount of sodium was also introduced with sodium fluorosilicate, which was present in the batch.

Some of the sodium oxide (0.6%) was introduced as Na_2SO_4 into the batch for experimental melting No. 3; this corresponds to adding 0.77% SO_3 . Melting No. 4 was conducted without adding sodium sulfate. All other conditions of founding and the granulation of the melt — holding temperature and time, air and gas ratio on the burner — were kept unchanged.

The frit and the poured-off sample from melting No. 4 had a brown hue, which indicates partial reduction of the titanium oxide, and the samples of melting No. 3 had a negligible grey-blue hue.

Differential-thermal analysis of the vitreous enamel powders did not show any substantial differences in the crystallizability of the samples from meltings Nos. 3 and 4. The whiteness of the coating based on glass enamel, melted together with Na_2SO_4 as an additive, turned out to be 2–3% higher than for the enamel with no additive. The other properties of the glass enamels from the foundings Nos. 3 and 4 had close values (see Table 1).

The calcination interval for the coatings of both casts lies in the range $760\text{--}840^{\circ}\text{C}$, and the whiteness depends on the calcination temperature (Fig. 1). Evidently, in the entire calcination temperature range the whiteness of the coating based on the enamel containing sulfur oxides is higher than that of enamels without additives. X-ray phase analysis of the heat-treated glass enamel powders showed that anatase crystallizes in a wide temperature range (Fig. 2), and the maximum anatase concentration is observed in samples heat-treated at $700\text{--}750^{\circ}\text{C}$. For higher heat-treatment temperatures ($800\text{--}850^{\circ}\text{C}$) the anatase concentration is somewhat higher in the enamel containing sulfur oxides than in the enamel without additives.

The higher degrees of whiteness of the enamels melted together with Na_2SO_4 as an additive are due to the more intense crystallization of anatase during calcination of the coating and, apparently, the neutralization of the negative effect

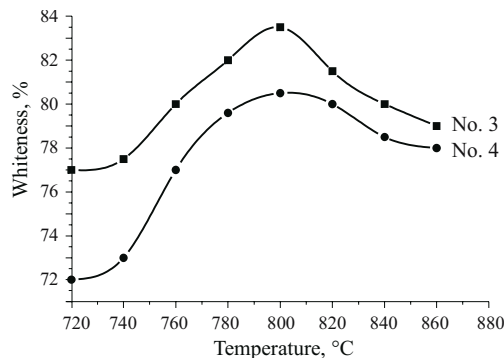


Fig. 1. Coating whiteness versus temperature of calcination: No. 3) the enamel was melted together with Na_2SO_4 as an additive; No. 4) enamel without Na_2SO_4 added.

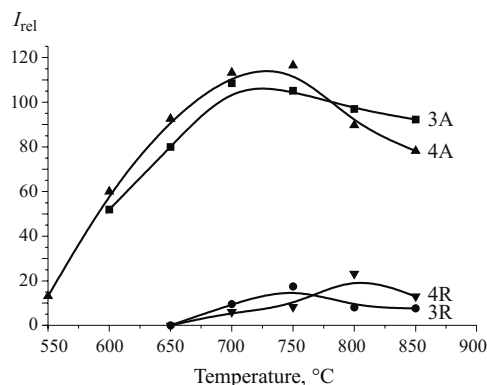


Fig. 2. Effect of the treatment temperature on the relative concentration of rutile (R) and anatase (A) in the vitreous enamel: 3A and 3R) enamels melted together with Na_2SO_4 as an additive; 4A and 4R) enamels without Na_2SO_4 added.

of the iron oxides as a result of the higher oxidation-reduction potential of the batch containing sodium sulfate.

In summary, the introduction of sodium sulfate into the batch of the titanium-containing glass enamel stimulates, during calcination of the coating, more intense crystallization of the titanium dioxide in the anatase form, which increases the whiteness of the coating. This effect is especially strong when raw materials (silica sand) with an elevated content of iron oxides are used. The introduction of sodium sulfate into the batch of the vitreous enamel makes it possible to create a more stable melting regime and to maintain a stable oxidation-reduction potential of the batch, which gives better reproducibility of the coating properties from one melting to another.

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